Thermodynamic and electronic structure study of two pressure-induced stuctural phase transitions of $PdSe_2$: interconversion path and structural preferences between the CdI_2-, PdS_2- and pyrite-type structures.

C. Sortais-Soulard,[1,2] S. Jobic,[2] M.-H. Whangbo,[3] W. Crichton.[4]

[1]CEA/DPTA, BP12, 91680 Bruyères le Châtel, France. email : celine_sortais_soulard@yahoo.fr - [2] IMN, 2 rue de la houssinière, 44000 Nantes, France. - [3] Departement of Chemistry, North Carolina University, Raleigh, 27695-8204, USA. - [4] ESRF, BP 220, 38043 Grenoble Cedex.

Under ambient conditions, $PdSe_2$ adopts the PdS_2-type structure (o-$PdSe_2$). Its crystal structure at high pressure (up to 30 GPa) was investigated at 20°C and at 300°C by X-ray energy-dispersive diffraction. Le Bail refinements and *ab initio* calculations evidenced a solid-solid phase transition to the pyrite-type structure (c-$PdSe_2$), strongly related to the o-PdS_2 (**Fig.1**).[1]

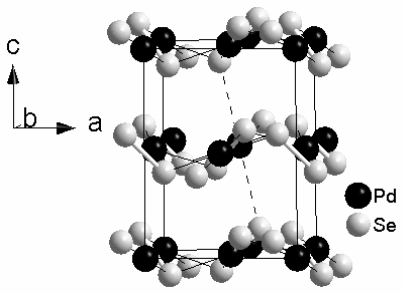

Fig. 1: perspective view of o-$PdSe_2$

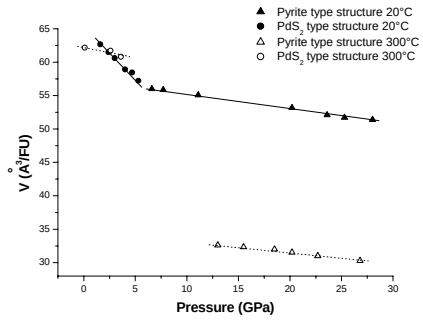

Fig. 2: plot of volume vs. pressure

Using the experimental data obtained at 20°C and 300°C, we examined the order of the $PdSe_2$ phase transition and its dependence on temperature. For this purpose, we calculated and analyzed the thermodynamical potential and the entropy generation by numerically calculating the equation of state. We also found that the cell volume of c-$PdSe_2$ was smaller at 300°C than at 20°C by nearly 40% (**Fig.2**). Such a dramatic decrease in the unit cell volume meant a strong reorganization of the bonding and was suggestive of an incoming phase transition. This possibility has been experimentally confirmed by fedgling high pressure experiments at ESRF. We surprisingly found that the new allotropic phase was a 2D CdI_2-type structure. It probed that all MSe_2 (M=transition metal) structures are linked. We evidenced the interconversion path between the 3 allotropes, explaining their relative stabilities on the basis of a thermodynamic and electronic structure study.

---

1 Larchev et al., Neorg. Mater. **1978**, *14*, 775 - C. Soulard et al., *Inorganic Chemistry*, **2004**, *43*, 1943.